

CANADIAN JOURNAL OF RESEARCH

VOLUME 24

MARCH, 1946

NUMBER 2

— SECTION B —

CHEMICAL SCIENCES

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NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

CANADIAN JOURNAL OF RESEARCH

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The *Canadian Journal of Research* is published by the National Research Council of Canada under authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. The *Canadian Journal of Research* is edited by a joint Editorial Board consisting of members of the National Research Council of Canada, the Royal Society of Canada, and the Chemical Institute of Canada.

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Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 24, SEC. B.

MARCH, 1946

NUMBER 2

THE HEAT CAPACITY OF AQUEOUS SOLUTIONS OF HYDROFLUORIC ACID¹

By T. THORVALDSON² AND E. C. BAILEY³

Abstract

The heat capacity of aqueous solutions of hydrofluoric acid varying in concentration from 0.55 to 48% was determined over the temperature range 18° to 20° C. The respective values for the specific heat varied between 0.996 and 0.718 cal. per gm. The values obtained are consistent among themselves but differ markedly from those found in the literature. The apparent molal heat capacity of the solute over this range of concentration and temperature was calculated and compared with values obtained from the data of other experimenters.

In connection with experimental determinations of the heats of formation of the aluminates and silicates of calcium, the authors found it necessary to determine the heat capacities of systems composed mainly of aqueous solutions of hydrofluoric acid over the temperature range 18° to 20° C. Calculations of the specific heats at 19° C. of solutions of hydrofluoric acid from these data gave values that differed considerably from those found in the literature (4, 6, 7). A series of determinations over a wide range of concentrations was therefore undertaken. The values obtained for solutions varying from 0.55% (HF·200 H₂O) to 48% (HF·1.20 H₂O) hydrofluoric acid are given below. The energy measurements were made in international joules and converted to defined calories by dividing by 4.1833.

Apparatus, Experimental Procedure, and Materials

The calorimeter system was of the adiabatic type, the copper submarine vessel enclosing the calorimeter being immersed in a large cylindrical tank, the temperature of which could be easily controlled by additions of hot or cold water with rapid mechanical stirring. The hydrofluoric acid was contained in a cylindrical vessel of fine gold, capacity about 750 cc., resting on inverted T-shaped ebonite supports and insulated from the copper submarine container by an air space about 6 mm. wide. The inside of the submarine vessel was coated with paraffin. The acid was stirred at a rate insuring temperature uniformity by a rotary stirrer (of an alloy 80% gold + 20% copper) thermally insulated from its shaft by a thin ebonite rod and operated

¹ Manuscript received September 11, 1945.

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by a small synchronous motor. The heating of the acid was effected by a small heater coil, of No. 34 constantan wire wound on a mica cross as described by Meyers (3), enclosed in a sealed nitrogen-filled platinum tube. The leads, made of No. 18 copper wire (No. 32 for portion inside calorimeter), were shielded against leakage currents. The heater system (resistance of coil about 50 ohms) was suspended by means of an ebonite tube through which the leads passed. Lead accumulators of large capacity and very constant voltage were used as the source of current.

The wiring of the potentiometer system was similar to that described by White (9, pp. 134-135), using standard resistances of 0.1 and 10 ohms calibrated by the U.S. Bureau of Standards, a type K Leeds and Northrup potentiometer, a sensitive galvanometer, and a calibrated Weston cell, making possible the measurement of both the current through the heater and the voltage across the heater at one setting of the potentiometer. The Weston cell was frequently compared with another calibrated cell. All the electrical equipment was placed on an equipotential shield.

The length of the heating period was measured by means of a stop watch, calibrated against a chronometer, the spring of the stop watch always having the same tension at the beginning of a run. The current was run through an external resistance of about 50 ohms for a 10 min. period before switching over to the calorimetric heater. Potentiometric readings were taken every minute during the run and the values obtained averaged. The usual heating period was about 12 minutes.

The temperature rise was measured by means of a Beckmann thermometer graduated in 0.01°C ., calibrated by the U.S. Bureau of Standards, and readings were easily estimated to 0.001°C . The relative calibration corrections over the range used were very small ($\pm 0.001^{\circ}\text{C}$. from the mean). Corrections were also made for setting and for exposed stem. The temperature of the outside bath was read by means of a similar thermometer. The thermometer exposed to the acid was protected by a closely fitting sheath of thin platinum foil, with any space between the platinum and the glass filled with mercury. During a run, the temperature of the outside bath was maintained at 0.010°C . above the temperature of the liquid in the gold calorimeter vessel. Transfer of heat due to this head was automatically included in the correction for stirring ("rating"), which was determined for at least one-half hour before and after each run. The temperature of the room varied only slightly during the whole series of experiments.

The "electrical energy equivalent" of the calorimeter was obtained by a series of nine determinations (made over the same temperature range by two different pairs of operators) in which a quantity of water of approximately the same heat capacity was substituted for the solution of hydrofluoric acid. The value used for the average heat capacity of water from 18° to 20°C . was that of Osborne, Stimson, and Ginnings (5), namely, 4.1817 int. j. per gm. per degree (0.9996 defined cal.). The value obtained for the "electrical energy equivalent" of the calorimeter was 44.6 j. (10.7 cal.) per degree.

As all the series of experiments with water and with the various concentrations of hydrofluoric acid were made under similar conditions, over the same range of temperature and with the same setting of the thermometer, errors peculiar to the apparatus tend to be eliminated in the final calculations of the specific heat of the acid.

A small error was probably introduced by the variation in the vapour tension of the acid solutions. It may be calculated that with pure water the heat required for the evaporation between 18° and 20° C. (into the 450 cc. of air saturated at 18° C. enclosed in the calorimetric system) is about 1 j. (0.25 cal.) per degree. This appears as a part of the "electrical energy equivalent" of the apparatus. With increasing concentration of acid the quantity of water evaporated during a determination of the heat capacity decreases slightly but this is partly offset by the evaporation of hydrogen fluoride. Vapour tension data for calculation of the error involved are not available. The error for the lower concentrations of acid is negligible, and, except perhaps with the highest concentrations of acid, is probably not greater than the mean precision error of the determinations.

The hydrofluoric acid was a commercial product of the highest quality (A. C. S. Specifications) and was used without further purification. The acid, which assayed 48.13% HF, gave negative tests for chloride and

TABLE I
HEAT CAPACITY DATA FOR AQUEOUS SOLUTIONS OF HYDROFLUORIC ACID*

Concentration of hydrofluoric acid				No. of determinations	Heat capacity C_p /gm./° C. (18° to 20° C.)			Apparent molal heat capacity of solute, cal.
%	Molality	Square root molality	Molal ratio H ₂ O/HF		International joules	Defined calories	$2\sqrt{\Sigma\Delta^2/n(n-1)}$, calories**	
48.13	46.37	6.81	1.20	3	3.005	0.7185	± 0.0012	8.31
34.95	26.81	5.18	2.07	7	3.235	0.7734	± 0.0010	7.04
25.10	16.75	4.09	3.31	5	3.470	0.8294	± 0.0008	6.29
19.97	12.47	3.53	4.45	6	3.599	0.8603	± 0.0004	6.05
14.96	8.791	2.96	6.31	4	3.730	0.8917	± 0.0004	5.57
10.02	5.565	2.36	9.97	5	3.873	0.9258	± 0.0004	5.28
5.26	2.775	1.67	20.00	7	4.014	0.9596	± 0.0004	4.79
2.173	1.110	1.05	50.00	4	4.110	0.9824	± 0.0001	4.15
1.459	0.740	0.86	75.00	3	4.134	0.9882	± 0.0002	4.32
1.086	0.540	0.74	101.2	4	4.150	0.9919	± 0.0005	5.8
0.551	0.277	0.53	200.3	4	4.165	0.9956	± 0.0005	5.4

* The weight of solution used in the calorimeter in the different series of experiments varied from 600 to 690 gm. with increasing concentration of acid. The temperature rise varied from 1.99° to 2.03° C., and the average final temperature varied from 20.02° to 20.10° C.

** This calculation of the "precision error" for each series of determinations gives a probability of 21 to 1 that the uncertainty of the mean experimental value does not exceed the limits indicated (8). $\Sigma\Delta^2$ is the sum of the squares of the individual deviations from the mean; n , the number of individual determinations in the series. Nine experiments with 600.64 gm. of distilled water in the calorimeter (heat capacity of water 18° to 20° C. = 600.64 \times 4.1817 or 2511.7 int. j./° C.) gave an average total experimental heat capacity of 2556.1 int. j./° C. or a calculated "electrical energy equivalent" for the apparatus of 44.6 j. The value of $2\sqrt{\Sigma\Delta^2/n(n-1)}$ for the series is 0.6 j. The values given in this column may therefore be considered to be the calculated "21:1" final "precision error" for each series.

sulphate, 0.002% non-volatile residue, and 0.03% fluosilicic acid (all tests according to A. C. S. Specifications for analytical reagents (1941)). Total acidity was determined by titration with carbonate-free sodium hydroxide, using a weight burette with phenolphthalein as indicator. Dilutions were made by weight and checked by titration after dilution. Paraffined glass vessels were used for handling the acid.

All weights were corrected to vacuum. The densities used in the calculations were obtained by interpolation from data given in International Critical Tables, and the atomic weights were the international values of 1941.

Experimental Results

Table I gives a summary of the significant data of the heat capacity determinations together with the calculated values for the apparent molal heat

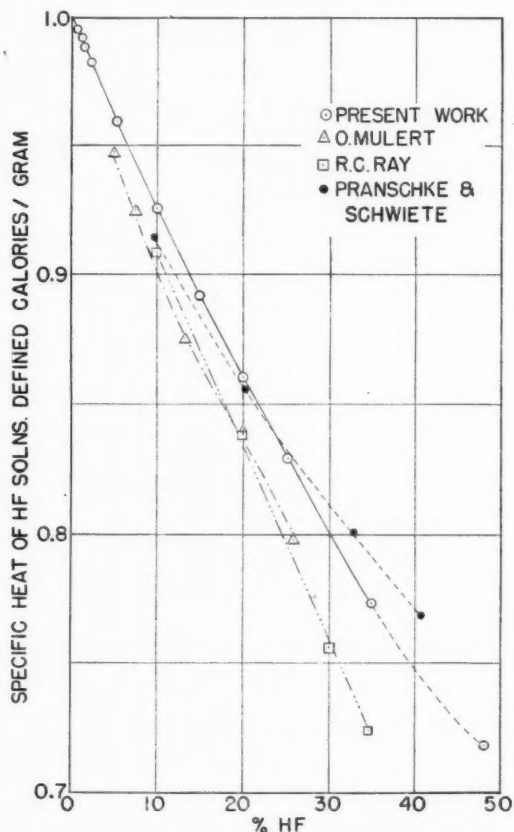


FIG. 1. Specific heat of solutions of hydrofluoric acid in defined calories per gram.

capacity of the solute. Fig. 1 gives graphically the specific heat data obtained in the present work and by previous investigators (4, 6, 7), and Fig. 2 the corresponding graphs for the apparent molal heat capacity of the solute plotted against the square root of the molality. In connection with the values for the apparent molal heat capacity of the solute in the two most dilute solutions, it should be noted that a change of less than 1 part in 1000 in the specific heat of the 1.086% solution and less than 1 in 3000 in the case of the 0.55% solution would bring the results into agreement with the other values on the graph.

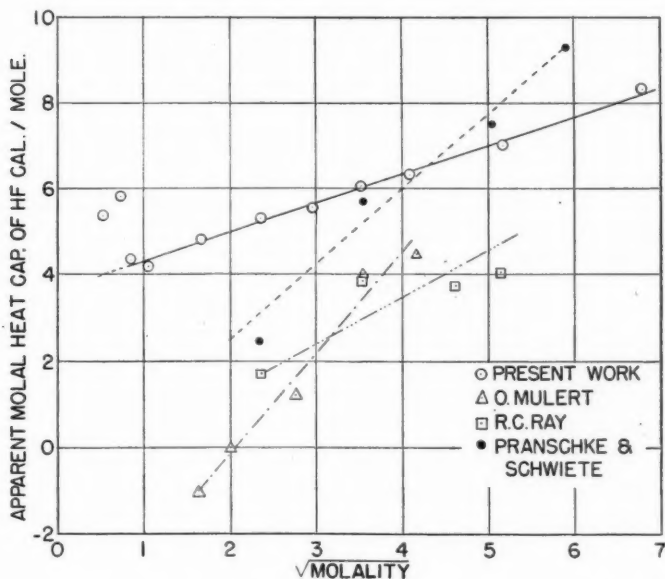


FIG. 2. Apparent molal heat capacity of hydrogen fluoride (HF) in aqueous solutions of hydrofluoric acid.

Discussion

In considering the plot of the apparent molal heat capacity of the solute against the root of the molality of the solution, it must be kept in mind that this gives a very sensitive method of comparing the consistency of the results. The curve for the data obtained in the present work shows that the results fall on a straight line except those for the two most dilute solutions. However, as already stated, the divergence represents less than 1 part in 1000 and 3000, respectively. It is also possible that these variations are significant, as Gucker and Schminke (2) obtained similar results with dilute solutions of hydrochloric acid.

The great variation between the results obtained by different experimenters as shown by these curves is rather disconcerting. It should, however, be

stated that in most cases very few details of experimentation were reported. Mulert states that the measurements were usually made from 17° to 18° C., Pranschke and Schwiete state that the values are for $18 \pm 1^\circ \text{C.}$, while Ray does not give the temperature range of the measurements.

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THE ALKALOIDS OF *LYCOPODIUM* SPECIES
VII. *LYCOPODIUM LUCIDULUM* MICHX. (*UROSTACHYS*
***LUCIDULUS* HERTER)¹**

BY RICHARD H. F. MANSKE² AND LÉO MARION³

Abstract

Nine alkaloids have been isolated from *Lycopodium lucidulum* Michx. Three of these, nicotine, lycopodine, and alkaloid L13, have been previously described. The remaining six are alkaloid L20 ($C_{17}H_{27}O_2N$), alkaloid L21 ($C_{13}H_{21}ON$), alkaloid L22 ($C_{16}H_{27}ON$), alkaloid L23 ($C_{16}H_{25}O_2N$), alkaloid L24 ($C_{16}H_{25}ON$), and alkaloid L25 ($C_{16}H_{25}O_2N$). These alkaloids represent but a small quantity of the total bases in the plant, the larger proportion of which it has not been possible to purify.

L. lucidulum Michx. is a more primitive plant than the other species of this genus that have been investigated. It exhibits the so-called "selago condition," a term used to indicate that the sporangia are borne in the axils of the leaves and not in a terminal spike as in most of the other Canadian species. Because of these and other characters *L. lucidulum* and related species have been relegated to a separate genus, namely, *Urostachys* Herter (5). Hutchinson and Wollack (1) have shown that the aluminium content of species of *Lycopodium* is much higher than that of species of *Urostachys* in Nessel's classification. With the single exception of *L. annotinum*, which is regarded as the most primitive of the genus, the aluminium content of the ash of lycopodiums may be as high as 20% and the aluminium in the dry plants often exceeds 0.1%. On the other hand, the aluminium in species of *Urostachys* seldom exceeds 0.1% and is occasionally less than 0.01%, amounts comparable to those normally present in other terrestrial plants. It was of interest, therefore, because of these characters of the plant to investigate the alkaloids it contains and ascertain what similarity might exist with those contained in the other species already studied.

A total of nine alkaloids have been isolated from *L. lucidulum*, three only of which, lycopodine, alkaloid L13, and nicotine, are common to other species. The ubiquitous lycopodine was found to be the major alkaloid and the second in importance is alkaloid L13, which is also present in *L. tristachyum* (3), *L. obscurum* (2), and *L. clavatum* (4). Nicotine was also isolated in small quantity.

The remaining alkaloids include alkaloid L20 ($C_{17}H_{27}O_2N$), alkaloid L21 ($C_{13}H_{21}ON$), alkaloid L22 ($C_{16}H_{27}ON$), alkaloid L23 ($C_{16}H_{25}O_2N$), alkaloid L24 ($C_{16}H_{25}ON$), and alkaloid L25 ($C_{16}H_{25}O_2N$). The quantities obtained of some of these alkaloids were very small considering the large quantity of

¹ Manuscript received September 27, 1945.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1354.

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plant used. Although the total quantity of ether-soluble bases amounted to 0.23%, the crystalline alkaloids isolated represent only about 0.05%. An even larger quantity of crude bases was soluble in chloroform but insoluble in ether. From this last quantity it has not yet been possible to isolate any homogeneous alkaloid.

Experimental

The plant material was collected in the neighbourhood of the Forestry Station at Duchesnay, north of Quebec City. Dried and ground it weighed 91.6 kgm. It was repeatedly extracted with cold methanol by percolation and the extract deprived of solvent by distillation in a steam-jacketed still. The thick syrup left after removal of the solvent was divided into a number of batches for convenience. The first batch was mixed with water, the mixture made acid to Congo with hydrochloric acid, heated on the steam-bath for 24 hr., and cooled. The voluminous insoluble material was filtered, heated again with dilute acid, and filtered cold. This second filtrate was added to the second batch, which was treated as the first. When the total extract had been thus treated the aqueous filtrates were basified with ammonia and exhaustively extracted with chloroform. The total base thus obtained was redissolved in dilute hydrochloric acid, the solution filtered through charcoal, extracted with ether (extract discarded), basified with ammonia, and repeatedly extracted with large portions of ether (Extract A). When ether failed to remove any more base, the extraction was continued with chloroform (Extract B).

Alkaloid L20

The combined ether extract A after evaporation yielded a thick gum (wt. 197 gm.), which partially crystallized on standing. This was stirred with an approximately equal volume of ether and the solution filtered to remove an insoluble crystalline residue, which was washed with ether and recrystallized repeatedly from boiling methanol from which it separated on cooling as colourless, elongated prisms; m.p. 259° C.*; wt. 1.0 gm. Found: C, 73.78, 73.78; H, 9.62, 9.56; N, 5.29, 5.26%. Calc. for $C_{17}H_{27}O_2N$: C, 73.65; H, 9.75; N, 5.05%.

Some of the above alkaloid was dissolved in methanol and the solution made just acid to Congo by the cautious addition of 65% perchloric acid. The crystalline perchlorate that separated on standing was recrystallized from methanol from which it separated as colourless prisms melting at 271° C. with previous discoloration. Found: C, 55.32, 55.11; H, 7.63, 7.48; N, 3.88, 3.81%. Calc. for $C_{17}H_{27}O_2N \cdot HClO_4$: C, 54.04; H, 7.42; N, 3.71%.

The ether filtrate from base L20 was evaporated to dryness and the residue fractionated *in vacuo*. It yielded the following fractions: I, b.p. up to 150° C. (20 μ), wt. 46 gm.; II, b.p. 150° to 170° C. (25 μ), wt. 10.5 gm.; III, b.p. 170° to 180° C. (25 μ), wt. 4.5 gm. A very large gummy residue was left that could not be distilled at that pressure without decomposition.

* All melting points are corrected.

Lycopodine

Fraction I was dissolved in acetone (70 cc.) containing methanol (2 cc.) and the solution made just acid to Congo with 65% perchloric acid. The crystalline perchlorate that separated was recrystallized once from boiling methanol and once from boiling water from which it separated in colourless prisms, m.p. 276° C. either alone or in admixture with a sample of lycopodine perchlorate. A quantity of this perchlorate was dissolved in hot water, the solution basified with ammonia, and the recovered base distilled *in vacuo* (b.p. 125° C. (20 μ)) and recrystallized from a little ether from which it was obtained as colourless prisms, m.p. 116° C. either alone or after admixture with lycopodine. The total weight of lycopodine obtained as perchlorate was 44.8 gm.

Alkaloid L13

The acetone mother-liquor from which the lycopodine perchlorate had separated was evaporated down to half its volume and the solution allowed to stand. A crop of crystals was deposited which was recrystallized from boiling methanol. This perchlorate melted at 274° C. and admixture with the perchlorate of alkaloid L13 failed to depress the melting point; wt. 20 gm. A quantity of this salt (5 gm.) was dissolved in boiling water, the solution basified with ammonia, and the recovered base crystallized twice from absolute ether. The base consisted of colourless flat prisms, m.p. 129° C., and in admixture with the base L13 (m.p. 130° C.) it melted at 130° C.

The acetone mother-liquor was diluted with water and heated on the steam-bath until the organic solvents were removed. The hot solution was then basified with ammonia, the mixture cooled, and extracted repeatedly with ether. The combined ether extract was distilled to dryness and the residue refractionated *in vacuo*: fraction *a*, b.p. 75° to 80° C. (0.3 mm.), wt. 0.14 gm.; fraction *b*, b.p. 85° to 90° C. (0.3 mm.), wt. 2.35 gm.; fraction *c*, b.p. 110° to 135° C. (0.3 mm.), wt. 5.79 gm.; fraction *d*, b.p. 150° to 180° C. (0.3 mm.), wt. 4.81 gm.; and fraction *e*, b.p. 180° to 200° C. (0.6 mm.), wt. 1.03 gm.

Nicotine

Fraction *a* obtained above consisted of a colourless oil which was dissolved in methanol and added to a methanolic solution of picric acid. A lemon-yellow picrate immediately separated, m.p. 226° C. either alone or after admixture with an authentic sample of nicotine dipicrate.

Alkaloid L21

Fraction *b* consisted of a slightly yellowish oil. It was dissolved in a little methanol and the solution cautiously neutralized with 65% perchloric acid. An equal volume of absolute ether was added to the solution, which was kept several hours in the refrigerator. The perchlorate which had crystallized was filtered, washed with a mixture of methanol and absolute ether, and recrystallized from the same mixture from which it formed aggregates of flat needles, m.p. 201° C. Found: C, 50.25, 50.28; H, 7.33, 7.29; N, 4.29, 4.33%. Calc. for $C_{13}H_{21}ON \cdot HClO_4 \cdot 0.5CH_4O$: C, 50.07; H, 7.42; N, 4.33%.

Some of the perchlorate was reconverted to the base, which was dissolved in methanol and added to a methanolic solution of picric acid. The solution was concentrated and allowed to stand. After several days a picrate separated, which, after one crystallization from methanol, consisted of long, soft, lemon-yellow needles, m.p. 107° C. Found: C, 52.64, 52.32; H, 6.07, 5.52; N, 12.98, 13.02%. Calc. for $C_{13}H_{21}ON \cdot C_6H_3O_7N_3$: C, 52.29; H, 5.51; N, 12.84%.

Fraction *c* was dissolved in methanol and the solution neutralized with 65% perchloric acid. A perchlorate crystallized out which proved to be that of lycopodine. The filtrate was diluted with water and heated on the steam-bath to remove the methanol. After several days at room temperature the aqueous solution deposited a quantity of crystals, which, after recrystallization from methanol-ether, melted at 201° C. and were identical with the perchlorate of alkaloid L21.

Alkaloid L22

Fraction *d*, b.p. 150° to 180° C. (0.3 mm.), was dissolved in methanol and neutralized with 65% perchloric acid. After a few days at room temperature the solution had deposited a perchlorate, which was filtered and recrystallized from boiling methanol (charcoal) from which it separated as small, colourless prisms, m.p. 254° C. with previous sintering. Wt. 1.5 gm. Found: C, 54.20, 54.83; H, 7.79, 7.88; N, 4.13, 4.03%. Calc. for $C_{16}H_{27}ON \cdot HClO_4$: C, 54.94; H, 8.01; N, 4.00%.

Some of the above perchlorate was dissolved in hot water and the solution basified with ammonia. After cooling, the precipitated base was extracted with ether. The base recovered from the ether was a colourless oil that crystallized on standing. It was recrystallized twice from petroleum ether by cooling in dry-ice-acetone. The base, obtained as colourless crystals, begins to sinter at 101° C. and melts at 108° C. Found: C, 76.93; H, 10.30; N, 5.73%. Calc. for $C_{16}H_{27}ON$: C, 77.11; H, 10.84; N, 5.62%.

Alkaloid L23

The combined mother-liquors from the recrystallizations of the perchlorate of L22 were evaporated down to a small volume and allowed to stand. A crystalline perchlorate was deposited which after several recrystallizations from a boiling mixture of methanol and ethyl acetate was obtained as colourless prisms, m.p. 300° C., wt. 0.9 gm. Found: C, 53.24, 53.07; H, 7.02, 7.31; N, 3.85, 3.86%. Calc. for $C_{16}H_{25}O_2N \cdot HClO_4$: C, 52.82; H, 7.15; N, 3.85%.

A small quantity of this perchlorate was dissolved in hot water and the solution basified with ammonia. The base was extracted with ether from the cooled solution and, after removal of the solvent, distilled *in vacuo*. It sublimed at 130° to 145° C. (0.2 mm.) as colourless prisms, m.p. 161° to 162° C. Recrystallization from petroleum ether did not alter the melting point. Found: C, 73.82; H, 9.99; N, 5.62, 5.41%. Calc. for $C_{16}H_{25}O_2N$: C, 73.00; H, 9.50; N, 5.32%.

Alkaloid L24

The mother-liquor from the crystallization of L23 perchlorate was diluted with water and the solution heated on the steam-bath until the organic solvent had evaporated. This solution, on cooling, deposited a mixture of crystals and gum, which was filtered and dissolved in hot methanol. The methanolic solution after some time deposited a crystalline perchlorate, which, when recrystallized twice more from methanol, was obtained as large, colourless feathery aggregates, m.p. 278° C., wt. 0.38 gm. Found: C, 55.86, 55.87; H, 8.14, 8.05; N, 4.09, 4.16%. Calc. for $C_{16}H_{25}ON \cdot HClO_4$: C, 55.25; H, 7.48; N, 4.03%. Admixture with lycopodine perchlorate depressed the melting point to 274° C.

Alkaloid L25

Fraction e, b.p. 180° to 200° C. (0.6 mm.) was dissolved in methanol, and the solution neutralized with 65% perchloric acid and kept in the refrigerator for several days. The perchlorate which had crystallized was filtered and recrystallized from boiling methanol from which it separated in short colourless needles, m.p. 297° C., wt. 0.3 gm. When mixed with the perchlorate of alkaloid L23, it melted at 260° to 265° C. Found: C, 52.47, 52.19; H, 7.38, 7.43; N, 3.69, 3.53%. Calc. for $C_{16}H_{25}O_2N \cdot HClO_4 \cdot 0.5 H_2O$: C, 52.18; H, 7.38; N, 3.69%.

The mother-liquor of this perchlorate yielded a further small quantity of alkaloid L23.

Fraction II from the original fractionation, b.p. 150° to 170° C. (25 μ), crystallized on standing. It was shaken with ether (30 cc.) until no more of the crystalline mass would dissolve. The mixture was filtered and the insoluble base recrystallized from methanol. It melted at 259° C. and was found to be identical with alkaloid L20. The ether filtrate was evaporated to dryness, the residue dissolved in acetone and the solution neutralized with 65% perchloric acid. After cooling in the refrigerator, a copious precipitate of a crystalline perchlorate had formed which was found to be identical with lycopodine perchlorate. The mother-liquor from the foregoing perchlorate was diluted with water and heated on the steam-bath until the methanol had evaporated. The solution was basified with ammonia and extracted with ether. The basic material obtained from the extract was fractionated *in vacuo*. It yielded several fractions from which further small quantities of nicotine and alkaloids L21 and L24 were isolated.

Fraction III, b.p. 170° to 180° C. (25 μ) consisted of a dark gum, which was shaken with ether and the solution filtered to remove some insoluble, amorphous material. The filtrate was evaporated to dryness, the residue dissolved in methanol, the solution neutralized with 65% perchloric acid and cooled in the refrigerator. The perchlorate which crystallized out was filtered and washed with methanol. It was identical with lycopodine perchlorate. The mother-liquor was concentrated on the steam-bath and again cooled in the refrigerator for several days in the course of which a second

perchlorate crystallized out. This was recrystallized from boiling methanol (charcoal) from which it separated as colourless prisms, m.p. 265° C. alone or in admixture with the perchlorate of alkaloid L20.

The chloroform extract *B* was dissolved in hot dilute hydrochloric acid, and the solution cooled, filtered through charcoal, and thoroughly extracted with ether. It was basified with ammonia and extracted with 15 large portions of ether and then with chloroform.

The ether extract was evaporated until the solution had reached a concentration of about 50%. On cooling, this deposited a further quantity of alkaloid L20. The ether filtrate was evaporated to dryness, and the basic residue dissolved in methanol and neutralized with 65% perchloric acid. This when worked up exactly as described for the main portion of the ether-soluble bases yielded further small quantities of the alkaloid perchlorates already mentioned.

In all cases the yield of alkaloid given is the total weight of that alkaloid or its perchlorate found in the plant. The weight of the ether-soluble alkaloids that could not be distilled below 200° C. at the pressures used is greater than that of the total alkaloids isolated either as crystalline bases or as their perchlorates. It has not yet been possible to induce crystallization of this relatively large quantity of amorphous base.

The quantity of ether-insoluble base which was extracted with chloroform is also very large and no success has so far been achieved in obtaining any tractable substance from it.

Acknowledgment

The plant material used in this investigation was placed at our disposal by Prof. P. L'Ecuyer of Laval University, Quebec, to whom we express our best thanks.

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THE ALKALOIDS OF *LYCOPodium* SPECIESVIII. *LYCOPodium SABINAEFOLIUM* WILLD.¹BY LÉO MARION² AND R. H. F. MANSKE³

Abstract

A total of four alkaloids have been isolated from *Lycopodium sabinaefolium* Willd. Three of these have already been found to occur together in other species, while the fourth, alkaloid L26 ($C_{15}H_{23}ON$), appears to be new.

In continuation of a series of researches on the alkaloids of *Lycopodium* species, an investigation of *Lycopodium sabinaefolium* Willd. is now reported. This plant, which does not appear to be as plentiful as some of the species already studied, contains four alkaloids. Three of these, i.e., lycopodine, alkaloid L13, and nicotine have already been found to occur together in *L. tristachyum* (3), *L. clavatum* (4), and *L. lucidulum* (2). The fourth, alkaloid L26 ($C_{15}H_{23}ON$), has not been found in the other species investigated so far. It is noteworthy that alkaloid L26 is the first C_{15} -alkaloid isolated in the *Lycopodium* series. Lycopodine is the main alkaloid occurring in this plant, while alkaloid L13 is obtained in a yield about half that of the former.

The plant material was identified by Mr. C. A. Weatherby of the Gray Herbarium, Harvard University, and by Dr. H. A. Senn of the Division of Botany and Plant Pathology, Central Experimental Farm, Ottawa, who were consulted independently, and the opportunity is taken to express grateful thanks.

Experimental

L. sabinaefolium Willd. was collected in late summer in the neighbourhood of Lake Timiscaming, in northern Quebec, by Mr. J. N. Chabot of the Department of Agriculture of the Province of Quebec to whom the authors acknowledge their indebtedness. The dried and ground plant weighed 1600 gm. It was extracted in Soxhlets with methanol and the solvent largely distilled from the combined extract. The residue was diluted with water and made acid to Congo by the addition of a slight excess of hydrochloric acid. The mixture was heated for 16 hr. on the steam-bath, cooled to room temperature, and subsequently in the refrigerator. It was filtered and the insoluble matter heated again with dilute hydrochloric acid and treated similarly. The combined filtrate was basified with ammonia and exhaustively extracted with chloroform.

The base obtained on evaporation of the chloroform was redissolved in warm, dilute hydrochloric acid and the solution filtered with suction through

¹ Manuscript received November 24, 1945.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1355.

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a layer of charcoal. The filtrate was thoroughly extracted with ether, made definitely basic with ammonia, and extracted first with five portions of ether and then with five portions of chloroform. From the combined ether extract a thick residual oil was obtained, wt. 2.2 gm., while the chloroform extract yielded a dark gum, wt. 1.0 gm. The combined weight of crude base represents a yield of 0.2%.

The dry ether-soluble base (2.2 gm.) when fractionated *in vacuo*, yielded the following fractions: I, a slightly yellowish oil, b.p. 135° to 140° C. (0.35 mm.), wt. 1.96 gm.; II, yellowish oil, b.p. 141°-145° C. (0.35 mm.), wt. 0.216 gm.; and a small undistilled residue. Both fractions I and II crystallized on cooling.

Lycopodine

The crystalline base obtained as fraction I was dissolved in boiling dry ether and the solution allowed to stand. It deposited beautiful colourless prisms, m.p. 116° C.* either alone or in admixture with an authentic specimen of lycopodine. The mother-liquor was evaporated to dryness and the residual oil dissolved in acetone. This solution was made just acid to Congo with 65% perchloric acid. After an hour the crystalline perchlorate which had started to separate almost immediately was filtered and washed with methanol. It melted at 283° C. and admixture with lycopodine perchlorate failed to depress the melting point. The total weight of base obtained as such or as perchlorate was 1.73 gm.

Alkaloid L13

The acetone solution from which lycopodine perchlorate had crystallized, when concentrated to half its volume and cooled, deposited a further small quantity of lycopodine perchlorate. The final mother-liquor was diluted with water and the solution heated on the steam-bath until the organic solvent had evaporated. After cooling, this solution deposited a crystalline perchlorate, which was filtered and recrystallized from boiling methanol. It separated in aggregates of colourless small rhombs, melting at 274° C. either alone or in admixture with the perchlorate of alkaloid L13. The total weight of this base obtained was 0.49 gm. Some of this perchlorate was dissolved in hot water, the solution basified with ammonia, and the precipitated base extracted with ether. The base recovered from the extract was recrystallized from ether and obtained as colourless prisms, m.p. 130° C. Admixture with alkaloid L13 failed to depress the melting point.

Fraction II, b.p. 141° to 145° C. (0.35 mm.) was dissolved in methanol and the solution made just acid to Congo with 65% perchloric acid. On standing, small colourless prisms were deposited, m.p. 275° C. Admixture with the perchlorate of alkaloid L13 failed to depress the melting point. Water was added to the mother-liquor, which was heated on the steam-bath until the methanol had evaporated. This aqueous solution was combined with the final aqueous mother-liquor from the alkaloids of fraction I, basified

* All melting points are corrected.

with ammonia, and exhaustively extracted with ether. The combined ether extract was distilled to dryness and the residual oil refractionated *in vacuo*. A very small first fraction was obtained as a colourless oil, b.p. 85° to 95° C. (0.6 mm.) and the bulk as a thick oil, b.p. 135° to 145° C. (0.6 mm.), which crystallized on standing.

Nicotine

The small fraction of oil (b.p. 85° to 95° C. (0.6 mm.)) obtained was dissolved in methanol (1 cc.) and added to a solution of picric acid in methanol (1 cc.). The resulting solution was evaporated to about half its volume and allowed to stand. It deposited a picrate as lemon-yellow prismatic needles, which, when dried, weighed less than 1 mgm. Mixed with an approximately equal quantity of an authentic specimen of nicotine dipicrate it failed to depress the melting point of the latter (226° C.).

Alkaloid L26

The refractionated base, b.p. 135° to 145° C. (0.6 mm.), was dissolved in dry ether, and the solution concentrated to a small volume and cooled in the refrigerator. It deposited a base in the form of small, stout, colourless prisms, which, after one recrystallization, melted at 171° C. In admixture with alkaloid L11 (m.p. 174° C.) (1), it began to sinter at 150° C. and was completely liquid at 158° C. Wt. 20 mgm. Found: C, 76.85; H, 10.61; N, 6.02%. Calc. for $C_{15}H_{23}ON$: C, 76.60; H, 10.64; N, 5.96%.

The base obtained from the original chloroform extract was fractionated *in vacuo* into two fractions, which were converted to perchlorates in methanol. Both yielded further quantities of the perchlorate of alkaloid L13.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XL. *CORYDALIS CORNUTA* ROYLE¹BY RICHARD H. F. MANSKE²

Abstract

Only protopine and *d*-stylopine have been isolated in amount sufficient for identification from *Corydalis cornuta*. Though closely related taxonomically to *C. sibirica* and *C. ochotensis* only the presence of acetyl-ornithine confirms this similarity. It is suggested that *C. ochotensis* is a polyploid form of *C. cornuta*.

For convenience in taxonomy the genus *Corydalis* has been subdivided into a number of sections and subsections. *Corydalis cornuta* Royle has been placed in the section *Eucorydalis* Prantl, subsection *Ramoso-sibiricae* Fedde along with *C. sibirica* (2) and *C. ochotensis* (4) whose chemical examination has already been recorded. There is ample morphological evidence to justify such a relationship. On casual examination *C. cornuta* appears to be a smaller form of *C. ochotensis* and like the latter it is an obligate biennial.

The three plants are the only ones known to elaborate acetyl-ornithine, an observation that lends support to the taxonomic evidence of similarity. It was therefore anticipated that at least some of the alkaloids found in *C. sibirica* or *C. ochotensis* would also be found in *C. cornuta*. Nevertheless, only the ubiquitous protopine was found in the three plants. Indeed, *C. cornuta* is unique in the genus *Corydalis*. It contains only a very small amount of total alkaloids and this consists largely of protopine. The only other alkaloid that could be isolated in amounts sufficient for identification was *d*-stylopine, which does not occur in the other two species mentioned. Minute quantities of two other bases were isolated, but neither was identical with bases already isolated from either *C. sibirica* or *C. ochotensis*.

It is obvious that, in view of the presence of acetyl-ornithine in this plant, it cannot be separated from the subsection *Ramoso-sibiricae*. It is equally obvious that the absence of characteristic alkaloids does not admit of such a classification unless a satisfactory explanation can be found. No such explanation is yet at hand but the writer ventures to suggest that *C. ochotensis* is a polyploid form of *C. cornuta*, and that for reasons not yet known the several forms are stable and persistent.

The writer is indebted to Dr. R. R. Stewart, Gordon College, Rawalpindi, India, who collected some plant material and supplied a quantity of seed from which the major portion of the material was grown. (The collection was made at an altitude of 7000 ft. on Naini Tal, Kumaon, U.P. India.) It is pertinent to note that the plant was grown in the same garden in which *C. sibirica* and *C. ochotensis* for previous investigations had been grown.

¹ Manuscript received November 5, 1945.

Contribution from the Research Laboratory, Dominion Rubber Company Limited, Guelph, Ont.

² Director of Research.

Experimental

There was available 400 gm. of the dried one-year-old roots and 11.3 kgm. of dried aerial portion. The acetyl-ornithine was isolated as described (3). A total of 6 gm. of purified amino acid was obtained.

The mother-liquors from the acetyl-ornithine were combined with the extract from the aerial portion and the whole worked up by the author's standardized procedure (1).

Protopine

The fraction BS yielded no other bases than protopine. It was recrystallized from chloroform-methanol until it melted alone or in admixture with an authentic specimen at 211° C.* The yield was about 0.03%.

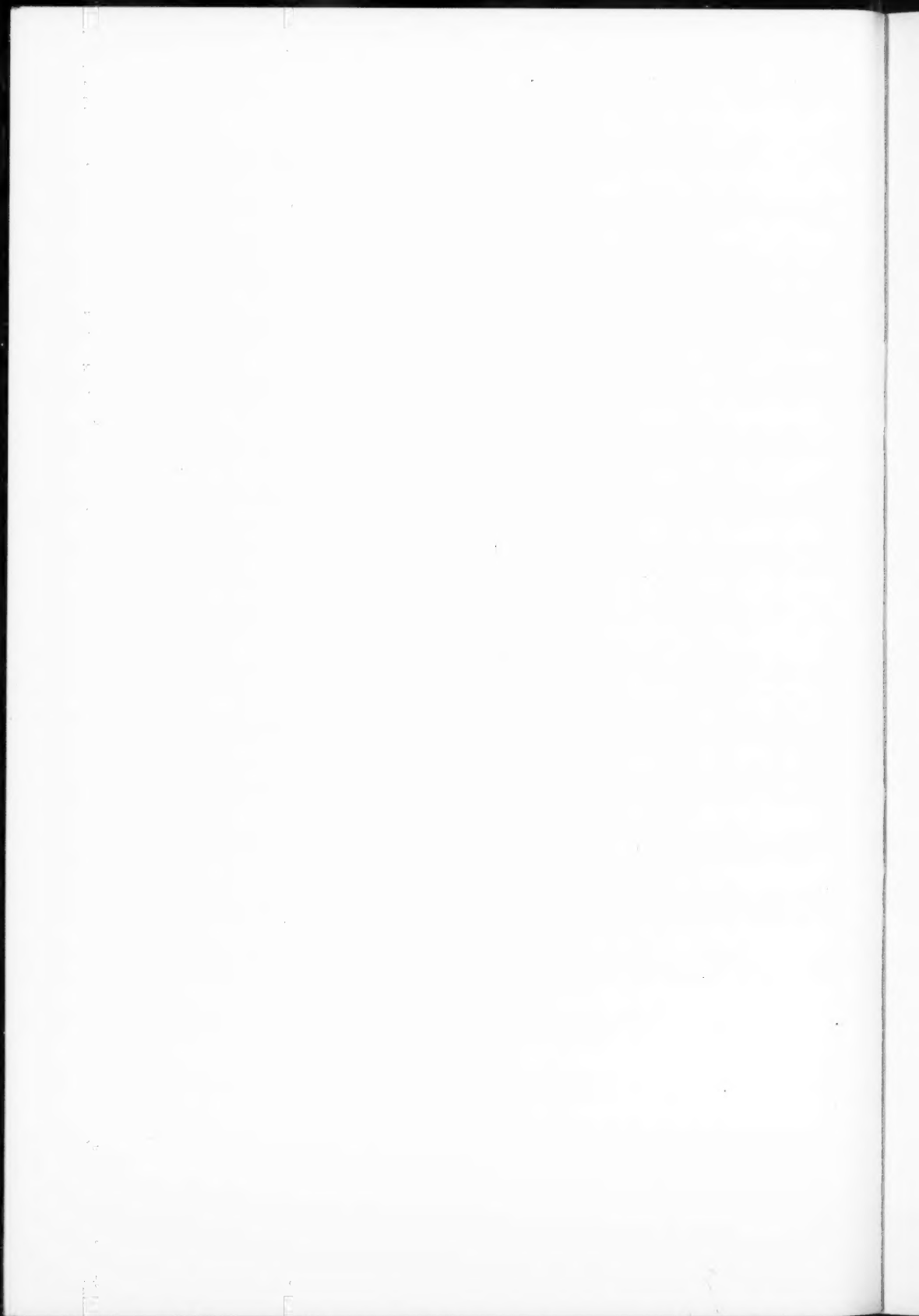
d-Stylopine

The fraction BC was redissolved in hot dilute hydrochloric acid and the filtered solution set aside. The colourless crystals of hydrochloride that separated were converted to free base and the latter recrystallized from hot methanol. The colourless needles thus obtained melted at 202° C. In admixture with *l*-stylopine it melted indefinitely at 206° to 220° C. It was obvious therefore that the base was *d*-stylopine and this was confirmed by recrystallizing equal amounts of this base and *l*-stylopine from chloroform-methanol. The brilliant colourless prisms thus obtained melted either alone or in admixture with authentic *dl*-stylopine at 223° C. The yield was about 0.02%.

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* All melting points are corrected.



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